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EFFECTS OF TEMPERATURE AND INTENSITY ON THERMODYNAMIC LIMITS FOR EFFICIENCIES OF PHOTOCHEMICAL CONVERSION OF SOLAR ENERGY

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EFFECTS OF TEMPERATURE AND INTENSITY ON THERMODYNAMIC LIMITS FOR EFFICIENCIES OF PHOTOCHEMICAL CONVERSION OF SOLAR ENERGY

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1. INTRODUCTION

The subject of thermodynamic limits on photochemical conversion of light to work has been of considerable interest for over twenty years. Recently, Ross and Hsiao (1) calculated quantum conversion efficiencies for solar radiation at air mass zero (AMO). Bolton (2) later extended this treatment to AM1.2 solar flux and also considered some kinetic as well as thermodynamic limitations. In this paper we apply these methods to a variety of solar intensities and absorber temperatures. We also examine improvements in efficiency which can be obtained by using systems with several absorbers of different effective band-gap wavelengths. The results, which are applicable to photovoltaic as well as to photochemical and photobiological conversion devices, represent absolute (i.e., ideal) upper limits on conversion efficiencies, analogous to Carnot efficiencies of heat engines.

All direct (i.e., quantum) conversion devices are threshold devices in that only photons with wavelengths up to that of the band-gap can be absorbed and converted to useful work. We assume that the excited electronic state created by absorption of a photon, whether in a semiconductor or in a photochemical system, has a sufficiently long lifetime (> 1 ps) that the excited state becomes thermally equilibrated with its environment. This assumption carries two consequences: first, the energy of the photon in excess of the band-gap is lost as heat; and second, the excited state loses all "memory" of the nature of the exciting radiation. Hence, only the flux of the absorbed photons is important.

We have also carried out calculations for two-photon processes (i.e., two discrete absorbers) over a limited range of temperature-intensity combinations. Finally, we have extended the treatment to calculate the optimum wavelengths for multiphoton cases ($3 \leq n \leq 8$) at fixed temperature and intensity.

2. METHOD

The equations derived by Ross and Hsiao (1) were incorporated into a BASIC software routine written for the Hewlett-Packard 9845-S desk-top computer system. The program was configured for variation of solar intensity from 1 to 10^4 suns at decadic intervals and absorber temperatures from 300 to 500 K in 50 K steps. As in Bolton's studies (2), the solar flux data of Böer (3) (AM1.2, "T/S") were used for all of these calculations. It should be noted, however, that Böer's spectra were computed using water-vapor absorption data which conflict with more recent models (4). This discrepancy creates a problem in the calculated solar spectrum in the region between 850 and 900 nm. Unfortunately, no reliable experimental solar spectra are currently available for comparison, so we have assumed that Böer's data yield a reasonable approximation to an AM1.2 solar spectrum.

The maximum fraction of solar power which can be converted to chemical energy (η_p) is the optimal energy storage rate (Eq. 12, Ref. 2) divided by the incident power integrated over the total solar spectrum. From these relationships, one can derive the functional dependence of η_p on intensity and temperature. The effects of these parameters were calculated for two-photon systems using the same assumptions as Bolton (2) for perfect, discrete absorbers. For each factor of 10 increase in solar intensity, we arbitrarily chose a 50 K temperature increment, using initial values of 1 sun and 300 K.

Starting at 300 nm, the wavelengths of the first (λ_1) and second (λ_2) photons were incremented according to the Böer spectrum (3) through 1500 nm, with the constraint $\lambda_2 > \lambda_1$. The output consists of the wavelengths for both photons and the corresponding power efficiencies (η_p). For the multiphoton calculations, the method of Davidon (5) for

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optimization of a smooth function involving many parameters was programmed into a CDC Cyber 170/720 computer. The program yields wavelength combinations for up to 8 photons that optimize the fraction of solar power which can be converted. For these calculations, the intensity and temperature were held constant at 1 sun and 300 K, respectively. As in the case of the single-photon calculations for these same conditions, our multiphoton results agree with the corresponding calculations of Bolton (2).

A word of caution in interpreting results from this program: The optimization routine finds only local maxima and is thus extremely sensitive to the starting conditions, especially for $n > 5$. The dimension of the optimization search is given by the number of photons, and each added dimension increases the "noise" in the area of the absolute maximum. Accordingly, for each value of $n > 5$, we carried out 4-5 optimizations with varying initial parameter estimates and chose from these the wavelength combination yielding the highest value of η_p.

3. RESULTS AND DISCUSSION

3.1 Temperature-Intensity Combinations

In general, the calculated thermodynamic (i.e., power) efficiencies for single-photon processes are a linear function of the logarithm of intensity at constant temperature and decrease linearly with increasing temperature at fixed intensity (Table 1). The advantage of utilizing

TABLE 1

Maximum Thermodynamic Efficiencies (single-photon) for AM1.2 Solar Radiation at Various Intensities and Absorber Temperatures (λ = 840 nm)

Intensity (suns)	Absorber Temperature (K)				
	300	350	400	450	500
1	32.3	30.2	28.1	26.1	24.0
10	34.1	32.3	30.5	28.7	26.9
10^2	35.9	34.4	32.8	31.3	29.8
10^3	37.7	36.5	35.2	34.0	32.7
10^4	39.5	38.5	37.6	36.7	35.7

concentrators for single-photon conversion devices to increase the intensity of incident radiation will be directly affected by the temperature increase incurred in the process; hence, if the intensity were increased by a factor of 10^3, the net gain in theoretical efficiency would be negligible if the absorber temperature were on the order of 500 K.

3.2 Two-Photon Systems

As shown by Bolton (2), absorption of multiple photons of different wavelengths can also increase the theoretical power efficiency of a quantum conversion device. Table 2 lists the effective wavelengths for maximum η_p with varying temperatures and intensities, and illustrates that the optimal wavelength combination for the two effective bandgaps is relatively insensitive to either absorber temperature or incident solar intensity. The maximum efficiency, however, is more strongly dependent on intensity than on temperature, at least for the limited range of conditions examined. As in the case of single band-gap systems, our calculations show that each 50 K temperature increment offsets the efficiency gain of a 10-fold increase of intensity. It would be interesting to extend this study to actual values of absorber temperatures experienced under concentrated solar radiation.

TABLE 2

Thermodynamic Efficiencies for Optimal Combinations of Two Absorber Wavelengths at AM1.2

Intensity (suns)	Temperature (K)	λ_1 (nm)	λ_2 (nm)	Efficiency η_p (%)
1	300	722	1318	43.6
10	350	722	1325	43.6
10^2	400	722	1325	44.6
10^3	450	722	1327	46.4
10^4	500	722	1339	49.3

3.3 Multiphoton Systems

The results of the optimization routine have been listed (Table 3) to illustrate the effect of the number of photons on the band-gap wavelengths and net power efficiency. Because the optimization routine does not calculate absolute maxima, there may be minor fluctuations in computed wavelength combinations and corresponding changes in efficiencies for higher order (i.e., $n > 5$) calculations, depending on the initial conditions. However, the absolute maxima for these cases need not be determined to exhibit the trends within the total data array. For instance, there exists a maximum η_p which appears to be ~60%, a value which is approached asymptotically with increasing number of photosystems (Figure 1).

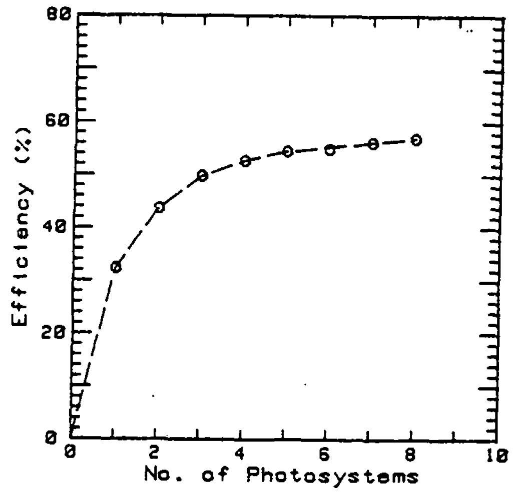

Fig. 1. Theoretical power efficiencies (η_p) for 1-8 ideal photosystems.

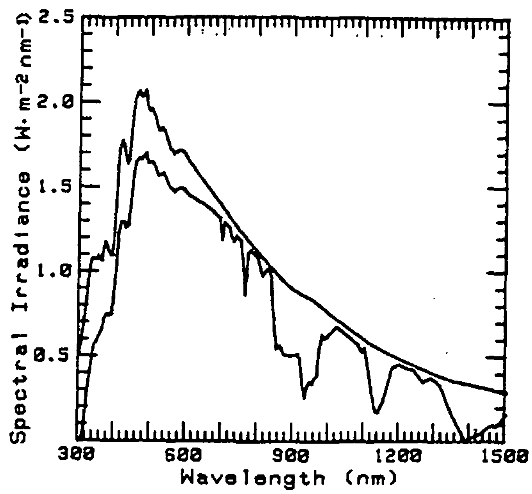

Fig. 2. Solar emission spectra at AM0 and AM1.2 (after Böer, Ref. 3).

These data suggest that in a functional device there will be a trade-off, probably around 2-4 photosystems, between the complexity imposed by an additional absorber and the net gain in efficiency.

Table 3

Optimum Wavelength Combinations and Corresponding Thermodynamic Efficiencies (AM1.2, 300 K)

n	Optimum Wavelengths (nm)								η_p (%)
1								843	32.3
2							722	1318	43.6
3						581	836	1333	49.7
4					510	669	853	1340	52.6
5				505	649	831	1081	1355	54.4
6			490	620	778	997	1189	1368	54.9
7		479	583	715	840	1024	1187	1378	56.2
8	436	518	611	719	852	1090	1268	1397	57.0

As the number of photosystems is increased, there is a strong blue shift in the optimal wavelength of the first photon. This is not, however, the case for the wavelength of the last photon (λ_n), which shows only a slight red shift from 1318 to 1397 nm on progression from 2 to 8 photons. A comparison of the data in Table 3 with the solar spectrum (Fig. 2) provides a logical explanation for the minimal trend in λ_n; for wavelengths longer than about 1380 nm, atmospheric conditions attenuate the photon flux, thus precluding the possibility of further energy gain with increasing wavelength.

Ireland, et al. (4) have treated the case of cascaded cells (n = 2,3,5,7), each with a discrete, narrow spectral response, and have calculated the maximum efficiencies as a function of the lowest band-gap energy. Although the calculated maxima were not presented, their graphical results (which were based on an assumed quantum efficiency of 0.9 as contrasted with 1.0 which we have assumed here) are in reasonable agreement with our data.

4. CONCLUSIONS

These multiphoton efficiencies represent theoretical thermodynamic limits which can be approached only with power conversion systems such as cascaded photovoltaic devices. The optimum wavelengths reported here should be useful in the design of such cells (6). In photochemical systems, for which energy storage is an important criterion, the optimum wavelengths and theoretical limits will differ considerably from the values listed in Table 3. As Bolton (2) has shown, the inherent chemical efficiency of a single-bandgap quantum-conversion device must be lower than the corresponding power efficiency. In addition, preliminary calculations on the storage efficiency of two-photon systems show that the effective band-gaps are significantly blue-shifted.

To date, our calculations have considered only AM1.2 solar flux data. For higher air mass, we anticipate further decreases in theoretical efficiencies accompanied by spectral shifts of the optimal wavelengths.

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